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17<sup>th</sup> June 2018

## **Platinum Nanoparticle Inclusion into a Carbonized Polymer of Intrinsic Microporosity: Electrochemical Characteristics of a Catalyst for Electroless Hydrogen Peroxide Production**

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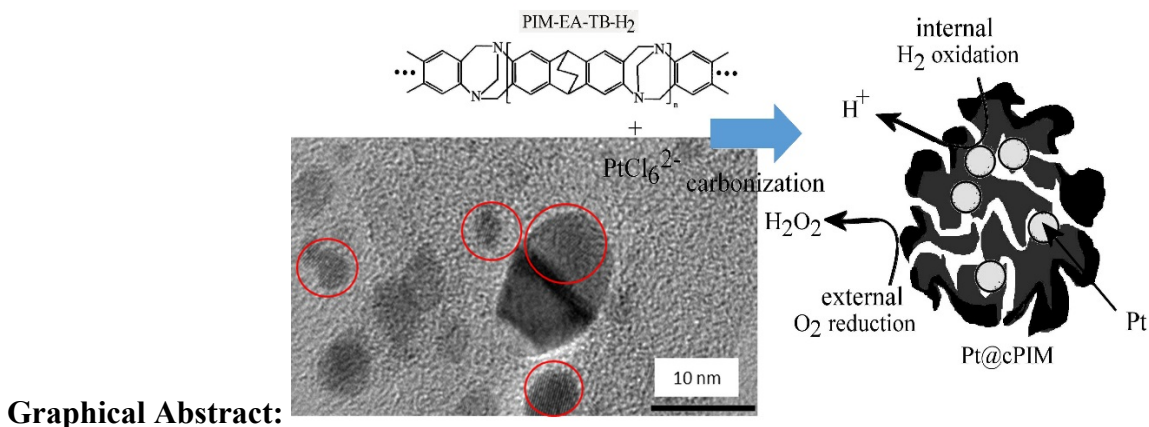
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## Abstract

The one-step vacuum carbonization synthesis of a platinum nano-catalyst embedded in a microporous heterocarbon (Pt@cPIM) is demonstrated. A nitrogen-rich polymer of intrinsic microporosity (PIM) precursor is impregnated with  $\text{PtCl}_6^{2-}$  to give (after vacuum carbonization at 700 °C) a nitrogen-containing heterocarbon with embedded Pt nanoparticles of typically 1-4 nm diameter (with some particles up to 20 nm diameter). The Brunauer-Emmett-Teller (BET) surface area of this hybrid material is  $518 \text{ m}^2\text{g}^{-1}$  (with a cumulative pore volume of  $1.1 \text{ cm}^3\text{g}^{-1}$ ) consistent with the surface area of the corresponding platinum-free heterocarbon. In electrochemical experiments the heterocarbon-embedded nano-platinum is observed as reactive towards hydrogen oxidation, but essentially non-reactive towards bigger molecules during methanol oxidation or during oxygen reduction. Therefore, oxygen reduction under electrochemical conditions is suggested to occur mainly *via* 2-electron pathway on the outer carbon shell to give  $\text{H}_2\text{O}_2$ . Kinetic selectivity is confirmed in exploratory catalysis experiments in the presence of  $\text{H}_2$  gas (which is oxidized on Pt) and  $\text{O}_2$  gas (which is reduced on the heterocarbon surface) to result in the direct formation of  $\text{H}_2\text{O}_2$ .



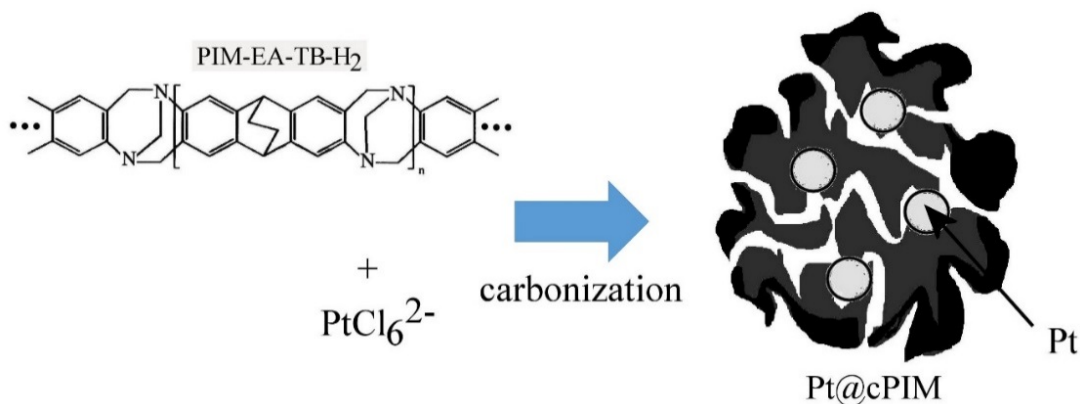
**Keywords:** heterocarbon; microporosity; voltammetry; peroxide; bifunctional catalysis

## 1. Introduction

Nanostructured and microporous composite materials offer new opportunities in catalysis and in electrocatalysis [1]. Electronic effects at the nanoscale affect surface reactivity [2] and can be combined with transport effects that occur in microporous channels and pores [3]. Recently, it has been shown that hydrophobic pore structures can lead to triphasic reaction conditions (for example in polymers of intrinsic microporosity or PIMs) and that these can also affect electrocatalyst reactivity [4]. In electrocatalysis particularly carbon-based nano-materials are important as illustrated by recently developed hetero-carbon materials based on nano-dots [5] and carbon nano-wires or tubes [6]. Access to novel carbon architectures can be achieved, for example, *via* microporous polymer precursors, which allow functionality such as fluorescence to be retained in the carbon [7] or molecular-scale microporosity to be preserved after gentle carbonization [8]. Polymers of intrinsic microporosity provide molecularly rigid and highly temperature stable precursor materials that retain porosity and morphology during carbonization [9]. This characteristic can be exploited in the preparation of new composite materials for catalysis.

Polymers of intrinsic microporosity (PIMs) have been developed [10,11] as a new class of molecularly rigid materials with applications in gas capture [12] and separation [13,14,15], electrochemistry [16], and in membrane technologies [17]. The rigid internal channel structure provides control over interactions with guest molecules/particles embedded within the intrinsic micropores with typical pore sizes in the 1-2 nm diameter range [18]. In this range of pore sizes exclusion effects may occur for some bigger molecules and mobility/diffusion effects may be linked to pore diameter and structure. Higher mobility can be achieved for smaller guest molecules such as H<sub>2</sub>. Based on their special properties, new applications of PIMs have been proposed. Recently, work has been reported focusing in areas such as selective battery membranes [19], fuel cell catalyst corrosion protection [20], enzymeless glucose oxidation [21], switchable membranes [22], triphasic electrocatalysis [23], and for ionic rectification devices [24].

The molecularly rigid microporous structure of PIMs causes interesting chemical behavior, for example imparting chemical stability under high temperature thermolysis conditions [8]. Thermolysis of metal-infused PIMs under high temperature conditions in air has been shown to yield for example nano-structured oxide materials [25]. Under vacuum carbonization conditions the backbone of the PIM material is believed to stay intact (for example for the PIM-EA-TB material [9]) even under conditions of partial carbonization to electrically conducting structures. The heteroatoms (e.g. here nitrogen) can be retained to give heterocarbon materials with high microporosity and with electrical conductivity [8]. Many of the recent studies on applications of PIMs in electrochemistry were based on PIM-EA-TB. The naming of PIM-EA-TB is based on the synthesis route, where an ethanoanthracene “EA” unit is coupled via Tröger Base “TB” coupling [26]. In this report a similar material, PIM-EA-TB-H<sub>2</sub>, is employed in which two methyl substituents at bridgehead positions have been replaced by hydrogen (see molecular structure in Figure 1).



**Figure 1.** Molecular structure of PIM-EA-TB-H<sub>2</sub> and schematic depiction of the adsorption of hexachloroplatin(IV)ic acid followed by mild vacuum carbonization to give a platinum nano-particle containing microporous heterocarbon.

The vacuum carbonization of PIM materials has been shown to provide novel microporous heterocarbon materials. For similar types of materials, there have already been suggestions for application in gas separation [27] and in water purification membranes [28]. The

electrochemical charging of the microporous carbonized structures has been shown to yield a high double layer capacitance but also pH dependent capacitance phenomena [9]. Two previous reports have indicated that pre-loading PIM-EA-TB with platinum [29] or with palladium [30] can lead to high surface area embedded catalyst materials with active metal nano-particles embedded in the microporous carbon host. A particular benefit arises from the fact that PIMs tend to not contaminate catalyst surfaces during carbonization and therefore additional catalyst activation treatments are not essential. Interest in novel carbon hosts [31] and porous carbon – platinum catalyst composites is strong for example in fuel cell catalyst development [32,33].

In this report hexachloroplatinic acid is adsorbed into PIM-EA-TB-H<sub>2</sub> to give a precursor material that is then vacuum carbonized (at 700 °C) to a novel catalyst hybrid material based on platinum nanoparticles in a microporous carbon. Both the degree of microporosity (controlling gas and charge diffusion) and the electrical conductivity of the material (allowing electron flow from inside to outside of catalyst particles) are shown to be important in the reactivity of the new host-guest catalyst. Electrochemical characterization suggests that only molecular hydrogen (H<sub>2</sub>) diffuses fast enough to reach the embedded catalyst to be oxidized. In exploratory catalysis experiments without external potential control, in the presence of a mixture of hydrogen and oxygen, hydrogen is oxidized to protons within the catalyst micropores, whereas the more bulky oxygen is reduced externally to give hydrogen peroxide in good yield.

## **2. Experimental**

### **2.1. Materials and reagents**

All solutions were prepared with deionized water of resistivity not less than 18.2 MΩcm resistivity taken from a Thermo Scientific water purification unit (ELGA). Methanol, isopropanol, perchloric acid (70%), phosphoric acid (85%), Nafion 117 solution (5% wt.), sodium dihydrogen phosphate (99%) were purchased from Sigma-Aldrich and used without further purification. Hexachloroplatinic acid (39.89%) obtained from Johnson

Matthey was used without purification. Laboratory grade (Pureshield) hydrogen gas and oxygen gas cylinders were obtained from BOC Ltd. Microporous polymer of intrinsic microporosity PIM-EA-TB-H<sub>2</sub> was synthesized following the literature recipe [26].

## 2.2. Instrumentation

Carbonisation was performed in a quartz tube linked to a vacuum pump (oil) in a TSH12 tubular furnace (Elite Thermal System Ltd.). Carbonized samples were characterized by transmission electron microscopy on a Joel JEM-2100 Plus TEM system with PED. Porosity analysis was performed with samples of 20 mg, which were degassed for six hours at 120°C prior to analysis. Analysis was carried with N<sub>2</sub> at 77 K on a Micrometrics 3Flex with P<sub>0</sub> measured continuously. Free space analysis with He was measured post-analysis. Recorded 80-point adsorption isotherm was analysed with density functional theory (DFT) method (N<sub>2</sub> at 77 K, cylindrical pore shape, NLDFT equilibrium model). Carbon monoxide (CO) chemisorption measurements were performed using a Quantachrome ChemBET TPR/TPD chemisorption analyser fitted with a TCD and 70 µL injection loop. Prior to chemisorption of CO, samples were pretreated (200 °C, 2 h) in a flow of H<sub>2</sub> (30 ml min<sup>-1</sup> STP). Platinum dispersion was calculated from total CO uptake assuming a 1:1 stoichiometry of adsorbed CO: surface Pt atoms [34]. Elemental analysis (obtained by Butterworth Laboratories Ltd., London) suggests for Pt@cPIM Pt 26 % C 55.07 % H 1.10 % N 4.75 %, which compares to the previously reported cPIM C 83.19 % H 2.46 % N 5.67 % [9].

Electrochemical characterization was performed with either an Ivium Compactstat potentiostat or a µAutolab type III potentiostat-galvanostat in a three-electrode configuration and in a conventional glass cell. A platinum wire was used as the counter electrode, KCl-saturated calomel (SCE, Radiometer) was used as the reference electrode, and catalyst modified 3 mm diameter glassy carbon disc electrodes (GC, BASi) were used as the working electrode.

### 2.3. Catalyst and electrode preparation

Powdered PIM-EA-TB-H<sub>2</sub> (21 mg) was first impregnated with platinum by immersion into an excess (10 mL) of 10 mM hexachloroplatinic acid solution in methanol. The sample was allowed to soak in the solution for 24 hours. The sample was then centrifuged (8000 rpm, 15 minutes), decanted and washed with 10 mL of water. The washing step was repeated and then the yellow-colored sample was left to dry at ambient temperature and pressure for 24 hours. Carbonization was performed at 700 °C for 3 hours in a custom-made evacuated quartz tube heated in a tubular furnace (in an oil pump vacuum of approximately 4 mbar). After cooling down a black powder is obtained.

Catalyst ink was prepared with 2 mg of carbonized material, which was homogenized by grinding (manually with mortar and pestle) together with 100 µL of Nafion 117 solution (5% wt.), then dispersed in 1 mL of isopropanol and sonicated for 15 minutes until fully homogeneous. A small volumes (between 5-15 µL as required) was drop-casted onto the 3 mm glassy carbon disk electrode and allowed to ambiently dry before electrochemical analysis.

### 2.4. Catalyst testing

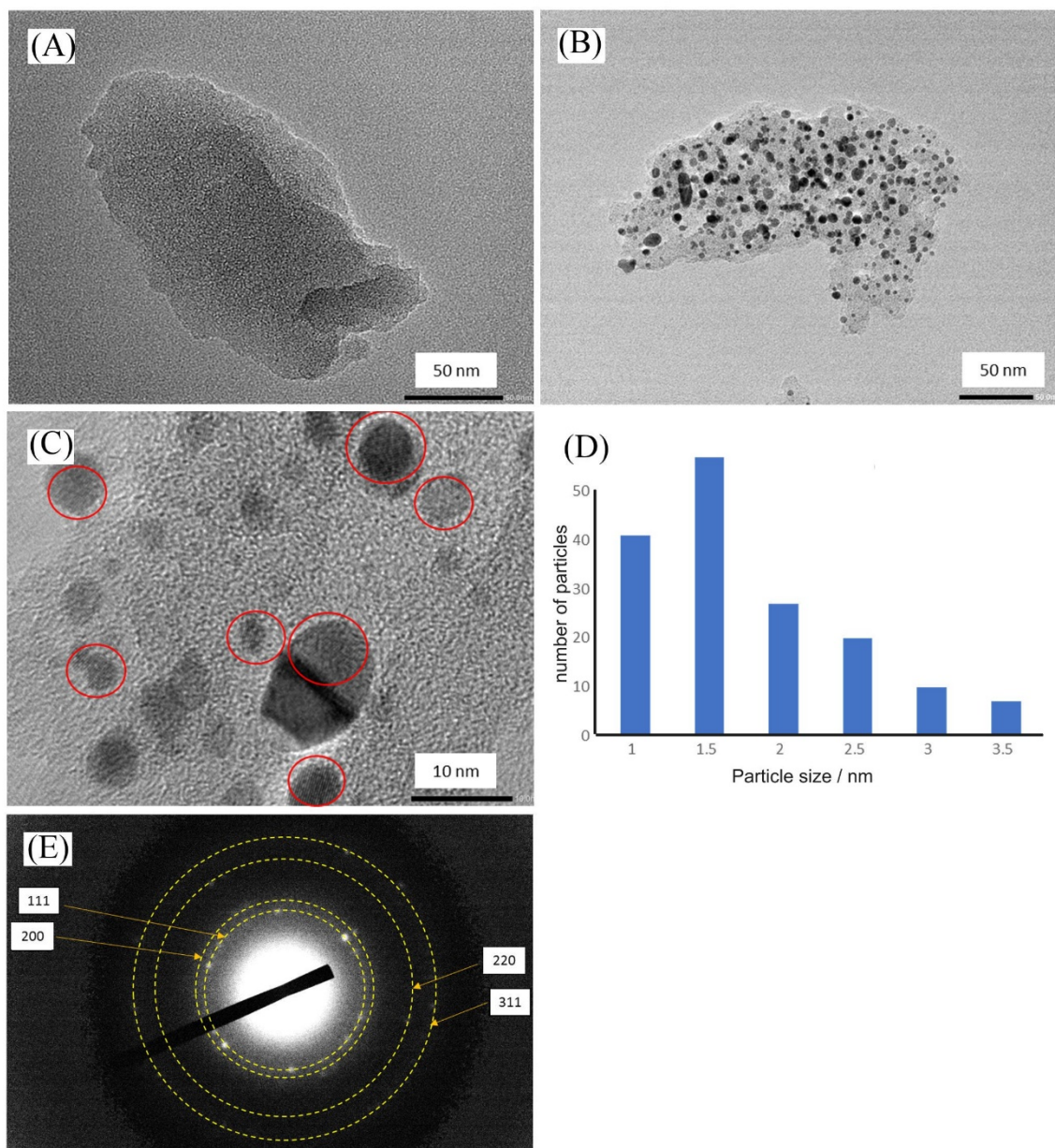
Catalysts were tested for their direct hydrogen peroxide synthesis activity using a stainless-steel autoclave (Parr). The 100 mL autoclave was fitted with a Teflon liner – nominal volume 66 mL. In a typical synthesis test, the autoclave was charged with catalyst (0.01g), water (2.9g) and methanol (5.6g), then purged with 5% H<sub>2</sub>/CO<sub>2</sub> three times before being filled with 5% H<sub>2</sub>/CO<sub>2</sub> (29 bar) then 25% O<sub>2</sub>/CO<sub>2</sub> (11 bar). The autoclave was chilled to 2°C before stirring at 1200 rpm for 30 min. After completion of the reaction H<sub>2</sub>O<sub>2</sub> formation is detected quantitatively.



### **3. Results and Discussion**

#### **3.1. Properties of Pt@cPIM I.: Structure and Porosity**

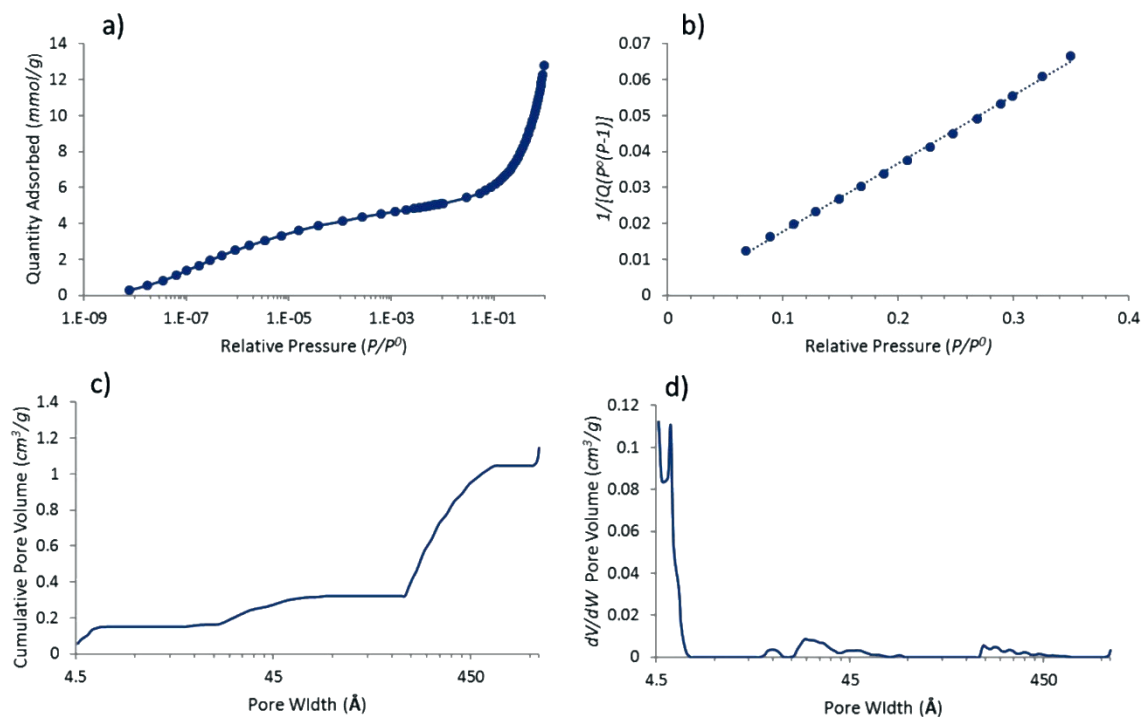
Successful impregnation of polymer by hexachloroplatinate precursor and formation of platinum nanoparticles during carbonization is confirmed by comparison of transmission electron microscopy (TEM) images of carbonized polymer PIM-EA-TB-H<sub>2</sub> without platinum (see Figure 2.A) and the new Pt@cPIM catalyst material (see Figure 2.). Particle size distribution data for platinum nanoparticles (see Figure 2.) show that the majority of particles falls into a 1-4 nm diameter size range with some bigger particles up to 20 nm. High magnification images reveal high crystallinity of platinum nanoparticles with clear presence of crystal lattice planes (see Figure 2.) consistent with platinum metal.



**Figure 2.** Transmission electron microscopy images for (A) carbonized PIM-EA-TB-H<sub>2</sub>, (B) carbonized PIM-EA-TB-H<sub>2</sub> with embedded nano-platinum, (C) high magnification micrograph showing platinum crystal lattice planes, (D) particle size distribution analysis, and (E) electron diffractogram with characteristic  $hkl$  reflections for platinum face centred cubic phase.

Electron diffraction data (Figure 2E) confirm the presence of crystalline platinum nanoparticles. Diffraction rings typical for platinum face centered cubic phase are observed. The thermolysis of PIM-EA-TB-H<sub>2</sub> without metal inclusion was reported recently [9] to give a similar material without platinum inclusion. Thermogravimetric data suggested that even up to 700 °C the weight loss was limited to about 26%. Both Raman spectra and electrochemical properties suggested that an electrically conducting sp<sup>2</sup>-carbon-rich material was formed. The nitrogen gas adsorption isotherm was reported indicative of a loss of Brunauer-Emmet-Teller (BET) surface area from 846 m<sup>2</sup>g<sup>-1</sup> for pure PIM-EA-TB-H<sub>2</sub> to 425 m<sup>2</sup>g<sup>-1</sup> for the carbonized PIM-EA-TB-H<sub>2</sub> (cPIM). However, the cumulative pore volume for the range from 1 nm to 5 nm remained similar before and after carbonization.

Gas adsorption and porosity characterisation was performed for Pt@cPIM based on the nitrogen adsorption isotherm at 77 K (Figure ). Data indicate at least partial retention of original microporous polymer structure in the carbonized Pt@cPIM catalyst material. This observation agrees with previous reports regarding vacuum carbonization of PIM-EA-TB at 500 °C [8]. The calculated BET surface area of 518 m<sup>2</sup>g<sup>-1</sup> (Figure ) is lower than the 846 m<sup>2</sup>g<sup>-1</sup> reported for the pure PIM-EA-TB-H<sub>2</sub> polymer and relatively close to the 425 m<sup>2</sup>g<sup>-1</sup> reported recently for the carbonised polymer without platinum [9]. The data imply that vacuum carbonization did not lead to a significant loss of small micropores. Impregnation of the polymer with the platinum precursor led to the formation of platinum nanoparticles without strongly affecting the properties of the microporous host carbon. Data from elemental analysis for Pt@cPIM (Pt 26 % C 55.07 % H 1.10 % N 4.75 %) confirm that nitrogen has been retained on an extent similar to that for the previously reported cPIM C 83.19 % H 2.46 % N 5.67 % [9].

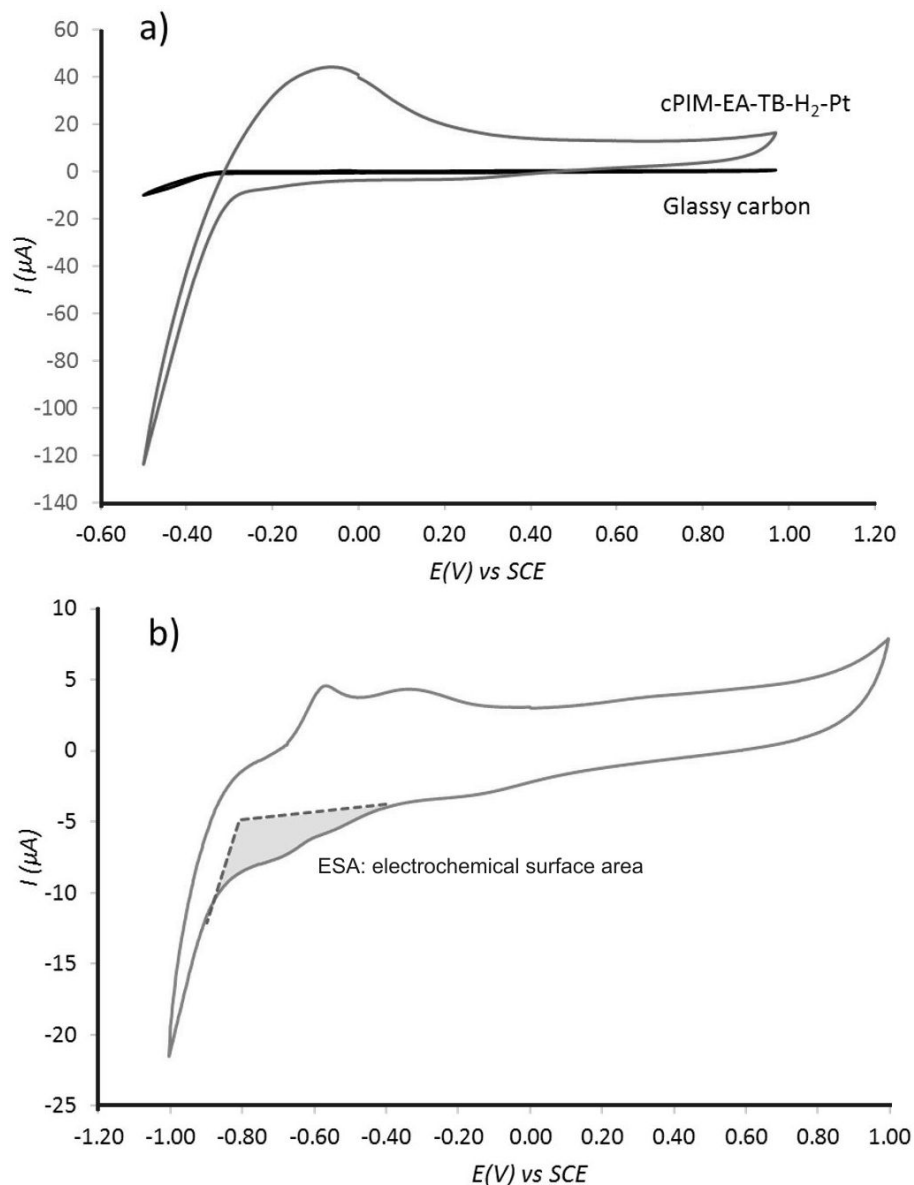


**Figure 3.** BET (77 K) nitrogen adsorption isotherm results for Pt@cPIM: (A)  $\text{N}_2$  adsorption isotherm; (B) BET analysis plot; (C) cumulative pore volume; (D) pore width distribution (NLDFT equilibrium for cylindrical pore model).

### 3.2. Properties of Pt@cPIM II.: Electrochemical Characterization

Electrochemical characterization was performed with 3 mm diameter glassy carbon working electrode, coated with a volume (5-15  $\mu\text{L}$ ) ink (see experimental) applied by drop-casting. The electrochemical activity of platinum embedded in the carbonized polymer is evident when Pt@cPIM voltammograms are compared with a voltammogram recorded in aqueous 0.1 M  $\text{HClO}_4$  for the bare glassy carbon electrode (Figure 4A). A substantial capacitive current component can be attributed to the microporous carbon and the distinct proton reduction and hydrogen oxidation response at -0.3 V vs. SCE clearly demonstrated catalytic activity.

Identification of characteristic hydrogen underpotential adsorption peaks [35] was not possible in acidic solution due to a high charging current generated by capacitive nature of cPIM-electrolyte interface. The presence of excess protons is believed to increase the double layer capacitance [9]. Therefore, the determination of the electrochemically active surface area for platinum (ESA) from the charge required to adsorb a hydrogen monolayer was estimated for an electrode immersed in 10 mM phosphate buffer solution at pH 7, where the hydrogen underpotential adsorption was more defined (Figure 4B). Estimation of electrochemically active surface area with  $ESA = \frac{Q_H}{210 \mu C cm^{-2}}$  (where  $Q_H$  is the charge required to remove hydrogen monolayer) gave a specific ESA of  $5.6 m^2 g^{-1}$ , which has to be regarded as a rough estimate. Additional experiments were performed employing carbon monoxide adsorption/desorption measurement (see experimental). In this case a value of the platinum surface area of  $2.15 m^2 g^{-1}$  was obtained in reasonable agreement with the electrochemical surface area estimate.



**Figure 4.** Cyclic voltammograms (3<sup>rd</sup> cycle, Ar saturated, scan rate 10 mVs<sup>-1</sup>) recorded in: a) 0.1 M HClO<sub>4</sub> solution; b) 10 mM phosphate buffer solution with highlighted hydrogen electrochemical underpotential adsorption region (grey).

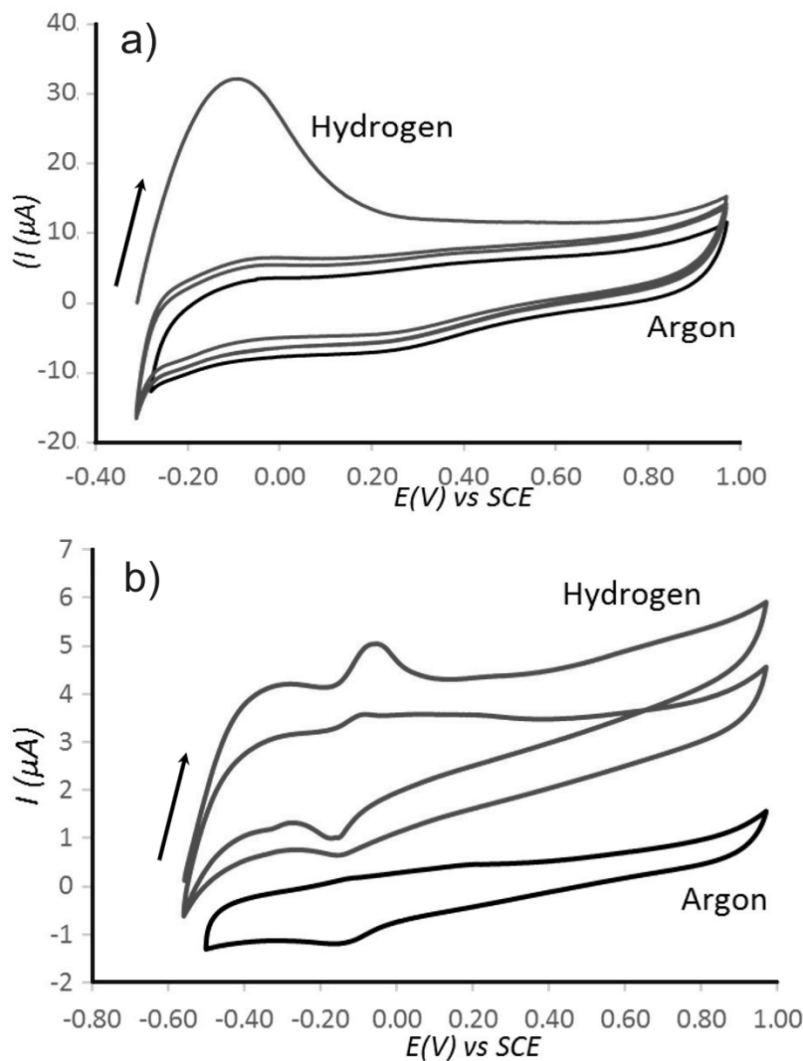
**Hydrogen Oxidation Reaction (HOR).** Hydrogen evolution [36,37,38] and hydrogen oxidation represent an exceptionally thoroughly studied class of electrocatalytic processes [39]. New types of catalysts are still being developed [40]. The electrocatalytic hydrogen oxidation was performed here with use of a catalyst ink drop-casted onto the glassy carbon electrode, which is then immersed into a hydrogen saturated 0.1 M perchloric acid solution

(Figure 5.) and into 10 mM phosphate buffered saline (PBS, pH 7) solution (Figure 5.). The process is assumed to occur via two-electron oxidation (Equation 1).



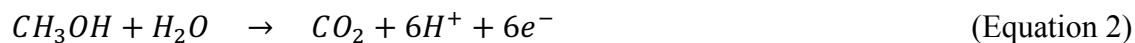
Cyclic voltammograms for hydrogen and argon saturated solutions were compared. Hydrogen oxidation is clearly observed at potential positive of approximately -0.5 V vs. SCE. Multi-cycle voltammograms in 0.1 M HClO<sub>4</sub> show an initial peak followed by constant hydrogen oxidation with about 3-4  $\mu$ A current. In phosphate buffer solution (Figure 5B) also the hydrogen underpotential adsorption peaks are clearly observed in voltammograms. Efficient hydrogen oxidation is reflected in a relatively high hydrogen desorption current at approximately -0.05 V vs. SCE. The hydrogen oxidation current is again approximately 3-4  $\mu$ A and therefore probably limited by hydrogen diffusion into the Pt@cPIM particles at the electrode surface.

From the capacitive current background response the specific capacitance of the Pt@cPIM material can be estimated as 5 Fg<sup>-1</sup> in neutral phosphate buffer solution and 27 Fg<sup>-1</sup> in 0.1 M perchloric acid. These values compare well with the recently reported value of 40 Fg<sup>-1</sup> for cPIM in 0.1 M perchloric acid [9].



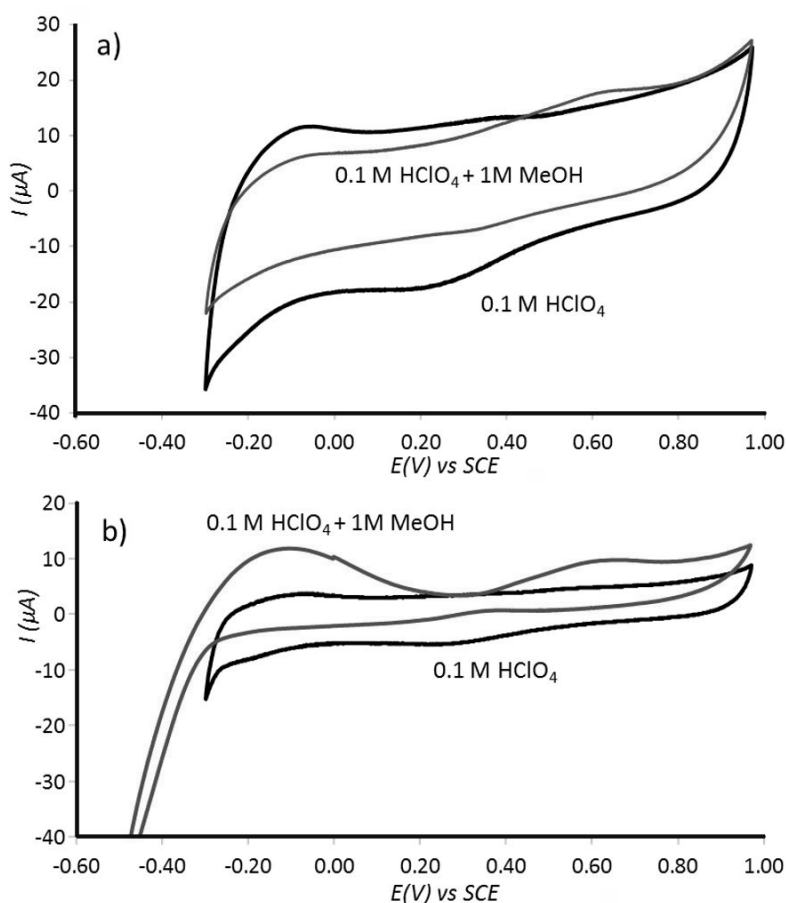
**Figure 5.** Cyclic voltammograms (scan rate  $10 \text{ mVs}^{-1}$ ) in a)  $0.1 \text{ M HClO}_4$  and b)  $10 \text{ mM PBS}$  solution purged with Ar or  $\text{H}_2$ .

**Methanol Oxidation Reaction (MOR).** The methanol oxidation reaction is investigated here as a model reaction important in many fuel cell applications. Although various types of catalysts systems have been studied [41,42], platinum has been shown in the past to be an effective catalyst for methanol fuel cells [43]. Methanol oxidation is a complex catalytic reaction with multiple reaction steps and an overall reaction shown in Equation 2.





Voltammograms for methanol oxidation recorded at  $0.1 \text{ Vs}^{-1}$  scan rate in aqueous  $0.1 \text{ M HClO}_4$  is presented in **Error! Reference source not found.**. Only a very minor methanol oxidation current peak is apparent at approximately  $0.7 \text{ V}$  vs. SCE in the forward cycle. At a lower scan rate the methanol oxidation can be identified more clearly (Figure 6B), but catalytic currents are obviously very low even for  $1 \text{ M}$  methanol. This result suggests a restricted access of methanol molecules to the platinum active sites and therefore high selectivity towards the smaller hydrogen molecules.

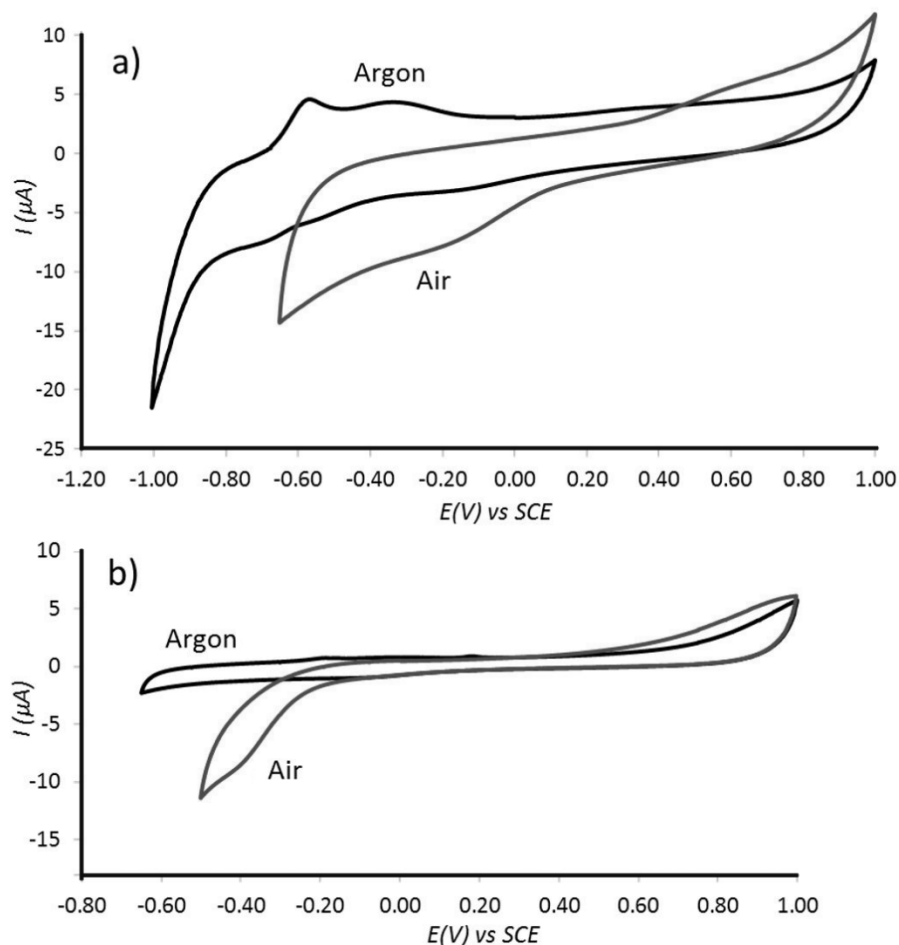


**Figure 6.** Cyclic voltammograms ( $3^{\text{rd}}$  cycle) in Ar saturated  $0.1 \text{ M HClO}_4$  without/with  $1.0 \text{ M}$  methanol recorded at a scan rate of a)  $100 \text{ mVs}^{-1}$  and b)  $10 \text{ mVs}^{-1}$ .

**Oxygen Reduction Reaction (ORR).** Oxygen reduction is a crucial processes in many areas of energy technology. Oxygen reduction catalysts have been developed based on noble metals, transition metals [44,45], oxides/hydroxides [46,47], and other types of materials. The ability to separate oxygen reduction from hydrogen oxidation is fundamental in fuel cells electrochemistry. Therefore, a selectivity of platinum nanoparticles embedded in microporous polymer towards oxygen electro-reduction was investigated with cyclic voltammetry experiment. There are two distinct reaction product linked to 4-electron reduction (Equation 3, predominant on platinum) and 2-electron reduction (Equation 4, predominant on carbon).



Catalyst ink material was drop-casted onto a 3 mm diameter glassy carbon disk electrode and immersed in oxygen saturated 10 mM phosphate buffer solution at pH 7 (Figure 7A). The oxygen reduction peak can be identified at approximately -0.4 V vs SCE and its magnitude suggests effective catalytic reduction. However, this reduction of oxygen occurs at very negative potential more typical for that of the 2-electron reduction on carbon materials [48]. This result is striking in that there is no catalytic ability of the platinum towards oxygen reduction under these conditions. High selectivity towards hydrogen is again achieved. The reduction of oxygen on carbon is likely to produce hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) instead of water.

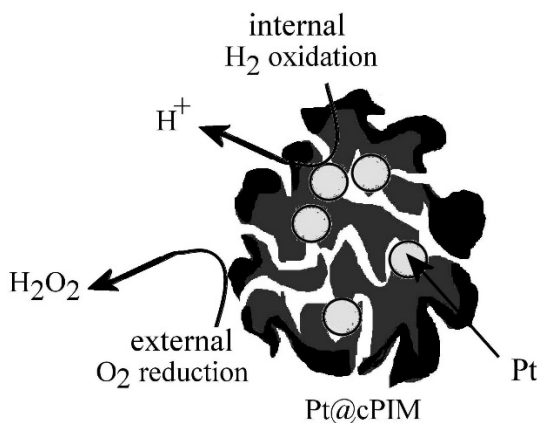


**Figure 7.** Cyclic voltammogram (3<sup>rd</sup> cycle, scan rate 5 mVs<sup>-1</sup>) for oxygen reduction in 10 mM phosphate buffer solution pH 7 purged with Ar or air.

### 3.3. Properties of Pt@cPIM III.: Catalysis and Hydrogen Peroxide Formation

Although electrochemical methods for hydrogen peroxide production are possible (e.g. based on driven fuel cells [49]), here the reactivity of the Pt@cPIM material is investigated for the direct catalytic conversion of hydrogen and oxygen to  $\text{H}_2\text{O}_2$ . The homogeneous-catalytic conversion of hydrogen and oxygen directly to hydrogen peroxide is of considerable interest and novel catalyst systems have been reported [50]. Figure 8 depicts the schematic reaction as a process in which molecular hydrogen is able to penetrate into the catalyst particles and react at the surface of the platinum particles. As a result, electrons are generated internally and conducted to the surface of the Pt@cPIM catalyst particle. The

oxygen reduction is believed to then occur only at the surface to give mainly  $H_2O_2$ . When evaluated for the direct synthesis reaction under standard catalytic reaction conditions, an activity of  $14 \text{ mol}_{H_2O_2} \text{ kg}_{cat}^{-1} \text{ h}^{-1}$  was achieved. This result is considerably higher than that observed for a 5wt% Pt/TiO<sub>2</sub> prepared by impregnation [51] and is comparable to the activity of some mono-metallic Pd catalysts, which tend to be most active for the direct synthesis reaction.



**Figure 8.** Schematic depiction of the catalytic process involving hydrogen and oxygen to give hydrogen peroxide.

#### 4. Conclusions

A novel composite catalyst has been prepared based on platinum nanoparticles embedded into a microporous heterocarbon. A one-step synthesis is employed based on the carbonization of a hexachloroplatinate loaded polymer of intrinsic microporosity (PIM-EA-TB-H<sub>2</sub>), which at 700 °C give the microporous catalyst with bi-functional reactivity and molecular size selectivity. The testing of catalytic activity is preliminary in nature and optimization of the catalyst performance based on Pt loading, carbonization temperature,

particle shape and size etc. is likely to be possible. Instead of a powder, the catalyst could be applied as a thin film on an inert substrate to be re-used or as part of a continuous reactor system.

More work will be needed to further develop the field of PIM precursors for heterocarbon materials. The intrinsic microporosity and thermal stability of PIMs allows highly interesting microporous hybrid materials to be obtained in a single step without activation and with embedded catalyst particles in an active state (the surface not blocked by the carbonization process). Catalysts could be developed for a wider range of applications.

### **Author Contributions**

Robert K. Adamiak performed most of the experimental work with some support from Naiara Hernández-Ibáñez (under supervision from Jesus Iniesta); Jennifer Edwards and Alexander G. R. Howe performed catalysis tests for hydrogen peroxide formation; Robert D. Armstrong and Stuart H. Taylor provided help with surface area and porosity experiments and analysis; Richard Malpass-Evans, Mariolino Carta, and Neil B. McKeown synthesized polymer of intrinsic microporosity precursor materials; Alberto Roldan, Yuanyang Rong, Daping He, and Frank Marken have supervisory roles and helped writing the manuscript.

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